



Catalytic decomposition of polystyrene. The role of acid and basic active centers

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ABSTRACT

The influence of the acid and basic properties of a catalyst on the selectivity of polystyrene transformation was studied. The properties of silicalumina $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%) doped with NaOH from 1 to 20 wt% and $\gamma\text{-Al}_2\text{O}_3$ containing 1 to 8 wt% NaOH or H_2SO_4 were examined using the test reactions of cumene (acid) and diacetone alcohol (base) transformation. These catalysts were used in polystyrene transformations. It was found that polystyrene decomposition involves thermal and catalytic transformation. In the first case, two main reaction pathways are involved: gradual depolymerization to the monomer (styrene) and pyrolysis leading to the formation of different volatile oligomers (dimers, trimers, tetramers.). The latter species react solely over the catalyst active centers. Linear dimers of styrene activated by Brønsted acid sites undergo decomposition to styrene and ethylbenzene as well as to toluene and α -methylstyrene. Consecutive transformation of the products leads to a simultaneous hydrogen (H^+ and H^-) production and coke formation. The latter ions are active in hydrogen transfer reactions which causes hydrogenation of styrene to ethylbenzene. In the presence of base catalysts selective styrene formation takes place and transformation leading to coke are slower hence ethylbenzene formation is suppressed. In the presence of acid catalysts linear dimers can also isomerize to cyclic derivatives which after dealkylation give benzene and methylindane. The later product in isomerization and hydrogen transfer reactions forms methylindene and naphthalene. The higher styrene oligomers reactions are catalyzed by both acid and basic sites leading mainly the monomer, i.e. styrene formation.

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1. Introduction

Plastic wastes constitute a growing serious problem such as the loss of natural resources, environmental pollution, and the reduction of landfill space. The management of plastic waste is intended for waste minimization, reuse, energy recovery and recycling. Two types of recycling can be distinguished: mechanical (material) recycling, which recovers the plastic material for similar or lower-quality applications for such plastics, and feedstock recycling which converts the plastic waste through chemical reactions into raw materials or fuels. The main components of the household plastic waste streams beside polyethylene, polypropylene, poly(vinyl chloride) and poly(ethylene terephthalate) include polystyrene and styrene copolymers. Presently, feedstock recycling only represents 2% of the total recycling effort, while mechanical recycling is the preferred recycling strategy (18%, 2008). The current unfavorable situation of feedstock recycling is caused by the high investment costs of recycling treatments [1]. Liquefaction, which converts plastics into hydrocarbon mixtures that are

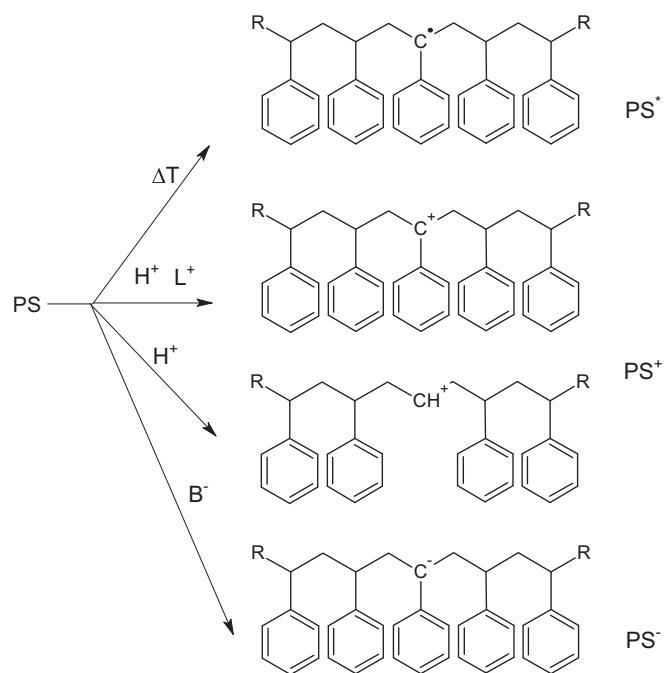
useful as fuels via thermal and/or catalytic cracking is receiving growing interest. Thermal processes comprise of thermal treatment of the plastic waste at 400–800 °C under inert atmosphere. Pyrolytic depolymerization of polystyrene is considered to be a radical process, which includes initiation, depolymerizing propagation, and radical coupling [2]. In the low-temperature range of 200–300 °C, thermal depolymerization of polystyrene results only in the reduction of the chain molecular weight, without the formation of volatile products [3]. At temperatures higher than 300 °C, volatile products and oligomers (dimers, trimers, etc.) are observed [4]. Larger amounts of volatile compounds, mainly toluene, ethylbenzene, cumene, styrene, naphthalenes, and indanes, were found at temperatures above 350 °C [5]. For neat polystyrene pyrolysis, conversion reached approximately 75% at 350 °C, whereas at 420 °C, the conversion reached a maximum of approximately 90% after 10 min of reaction and decreased to approximately 70% after 180 min [6]. Liu et al. studied the pyrolysis of polystyrene in a laboratory fluidized bed reactor in the 450–700 °C temperature range [7]. The yield of styrene reached a maximum of 78.7 wt.% at 600 °C. The uncatalyzed pyrolysis of polystyrene has been also reported by Williams and Williams to produce 83 wt.% conversion of a low viscosity oil consisting mainly of styrene, with a gas and char yield each of less than 5 wt.% [8].

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In catalytic processes the use of catalysts allows the plastic degradation pathway to be modified, with regard to pure thermal cracking. Initially, two positive effects are to be expected by the incorporation of a catalyst into the reaction medium: a reduction of the cracking temperature, and suitable control of the selectivity, which enables the formation of more-valuable products. Catalysts for plastic cracking may be either homogeneous or heterogeneous. Homogeneous systems are mostly based on classic Lewis acids, such as aluminum trichloride, metal tetrachloroaluminates, ferric chloride, boron trifluoride etherate, and tin(IV) chloride [9,10]. Homogeneous catalytic systems pose the problem because of the difficult recovery and separation of the catalysts from the products. In contrast, a great variety of heterogeneous catalysts have been used for the catalytic cracking of plastics: silica alumina [11–13], conventional zeolites (HZSM-5, HBeta, HY, etc.) [5,6,8,14–16], fresh and spent fluid catalytic cracking catalysts (FCC) [17–20], mesostructured catalysts (MCM-41, FSM-16, Al-SBA-15, AIUTD-1) [21,22], nanocrystalline and hierarchical zeolites [23], natural clinoptilolite zeolite [24] superacid solids ($\text{ZrO}_2/\text{SO}_4^{2-}$) [25], gallosilicates [26], aluminum pillared clays [27], metal-based catalysts [28], and basic oxides (BaO , K_2O) [29–32]. It should be noticed that latter basic oxides were successfully used in the degradation of polystyrene, which led to high selectivity to the monomer styrene. Typical mesoporous structure of $\text{K}_2\text{O}/\text{Si}-\text{MCM}-41$ molecular sieve was obtained by impregnating Si-MCM-41 with KNO_3 [33]. The authors claimed that such catalytic system indicated better catalytic activity than CaO , Si-MCM-41 and Al-MCM-41 catalysts. Guoxi et al. reported the effects of Al, Zn, Fe, Ni, and Cu powders on the thermal degradation of waste polystyrene. The results show that the catalytic effects of metal powders have a relationship with their activities. It is suggested that polystyrene degrades through a transient intermediate in the presence of metal powders, and the degradation of the transient intermediate is the rate-determining step [34]. The use of different acidic solids such as zeolites, alumina and silicaalumina as catalysts at 350 °C has been reported to significantly modify the selectivity, since the main products are benzene, ethylbenzene and cumene [35,36]. HMC-M-41 zeolite, compared to HZSM-5 and amorphous $\text{SiO}_2-\text{Al}_2\text{O}_3$, was the only catalyst exhibiting a slight increase in activity with regard to the thermal cracking of polystyrene at 375 °C [22]. The presence of zeolite ZSM-5 or a Y-zeolite was found to increase the yield of gaseous products, form a significant amount of carbonaceous coke and decrease the amount of oil obtained during the pyrolysis of waste polystyrene in a fixed bed reactor [37]. Other authors claimed that in the presence of ZSM-5 zeolite oil, which contained mostly single ring aromatics, such as toluene and ethylbenzene was produced [38]. The conversion of polystyrene was 90.5%, the yield of liquid products was 85.7%, and the yield of styrene reached 69%. The effect of fluid catalytic cracking (FCC) catalysts as a fluidized bed material on the polystyrene pyrolysis was examined by Mertinkat et al. [39]. de la Puente et al. found that in the catalytic cracking of polystyrene over a commercial FCC catalyst at 550 °C, both conversion and product distribution were practically the same as those obtained when feeding pure styrene [40].

In recent years polymer wastes biodegradation has been considered as a new way of plastic recycling. Synthetic polymers such as polystyrene are considered to be non-biodegradable [41]. To facilitate biodegradation of polystyrene a preliminary step of photo-oxidation or thermo-oxidation should be performed. This oxidation process results in the formation of carbonyl groups in the hydrocarbon chains those can be consumed by non-specific microorganisms [42]. However, only a few microbial strains are capable of degrading standard nonoxidized hydrocarbon polymers [43]. These include the actinomycete *Rhodococcus ruber* (strain C208) [44–46]. Since polystyrene is hydrophobic, forming a stable



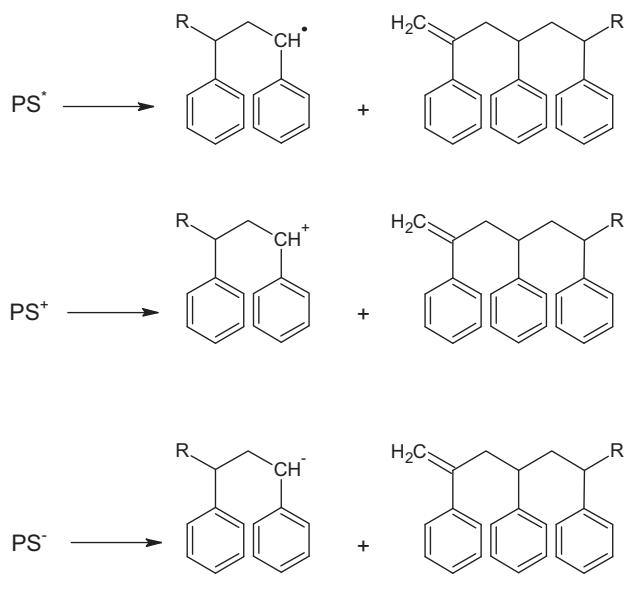
Scheme 1.

biofilm requires that the bacterial surface will also be hydrophobic. Sanin et al. reported changes in bacterial surface hydrophobicity in response to carbon starvation [47]. It was shown that with carbon starved culture bacterial isolates, including *R. corallinus*, became more hydrophobic and more adhesive than with non-starved cells. These findings may explain the high affinity of C208 cells for the polystyrene and raise the possibility that the low carbon availability in strain C208 cultures may also enhance hydrophobic interactions and biofilm development. Enzymatic degradation of polystyrene by hydroquinone peroxidase of *azotobacter beijerinckii* HM121 was described by Nakamiya et al. [48]. Biodegradation of polystyrene buried under soil for over 32 years were also reported by Otake et al. [49].

The variety of available experimental data allows to summarize the chemistry of polystyrene transformation. Degradation begins with the transformation of the polymeric chain into the radical, cationic or anionic transition states (Scheme 1).

The radical species formed by thermal activation, while cationic and anionic species counterparts a specific catalyst. Brønsted acid type catalysts can protonate the aromatic ring attached to the aliphatic chain of the polystyrene resulting in benzene elimination (dealkylation reaction) and the formation of a polycation [50]. A Lewis acid catalyst would detach a hydride anion from the benzylic position in polystyrene with a III order cation formation [10]. Basic catalysts activate polystyrene through deprotonation [51]. The next step of the transformation is a β-cleavage of the C–C bond located in the aliphatic chain. New radicals, cations or anions active in further reactions are then formed (Scheme 2).

They undergo depolymerization leading to styrene and shorter polymer fragments being II order radicals, cations or anions. Due to internal hydrogen (H^\bullet), hydrogen anion (H^-) or proton (H^+) shift from the end of the chain to the interior, they form II-nd order species whose decomposition results in the formation of styrene oligomers (dimers, trimers.) [29,30,50,52,53]. The latter compounds can isomerize and decompose into final polystyrene cracking products such as benzene, toluene, ethylbenzene, styrene, α-methylstyrene, cumene, indane, indene, naphthalene and others. The selectivity of the transformation depends on the nature of the catalyst. It is generally agreed that styrene and the other products



such as benzene, toluene, ethylbenzene, α -methylstyrene, cumene and derivatives of indane, indene and naphthalene are formed in the presence of acid type catalysts [50]. On the other hand the most favorable transformation in the application of solid bases is selective depolymerization to obtain styrene [29,53]. Detailed reaction mechanisms which have already been proposed dealt mainly with the transformations over Brønsted acids [50]. The first step is a polystyrene chain protonation to convert it to a reactive macro-cation which undergoes further decomposition. However, it is necessary to note that at elevated temperatures, 673 K and higher, typical for catalytic cracking, polystyrene also undergoes thermal decomposition [54]. Hence, the appropriate reactant should not be polystyrene, but rather a mixture of styrene oligomers. The mechanisms of polystyrene transformation over Lewis acids and solid bases are less documented.

The aim of the presented work was to study the changes in the selectivity of polystyrene transformation when the properties of the applied catalysts change gradually from acidic to basic. Silicaalumina $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%) dotted with NaOH from 1 to 20 wt% and $\gamma\text{-Al}_2\text{O}_3$ containing NaOH or H_2SO_4 from 1 to 8 wt% were chosen as catalysts. The introduction of sodium ions of solids surface is an effective way to both acid centers poisoning (neutralization) and basic sites formation [55]. Sulfuric acid treatment of alumina results in strong acid centers creation [56]. The acid strength of such sites could reach $\text{H}_0 = -12$ limit indicating that such system can be considered as solid superacid [56].

Two test reactions were used to monitor the evolution of acidic and basic properties of the used catalysts: cumene and diacetone alcohol transformation. In the presence of Brønsted acid centers cumene undergoes dealkylation into benzene and propylene as well as disproportionation into benzene and diisopropylbenzenes [57]. Under the influence of Lewis acid sites it reacts with ethylbenzene, p-cymene and n-propylbenzene formation [57]. The basic centers catalyze diacetone alcohol decomposition into acetone [58]. In the presence of the catalysts with defined acid-base properties, the transformation of polystyrene, styrene dimers and compounds being considered as transition reaction products were studied. The results should produce a more detailed illustration of polystyrene decomposition reaction scheme which takes into consideration the action of both temperature and the catalysts of different nature.

2. Experimental

2.1. Catalysts

The following solids were used as catalysts for polystyrene transformation: MgO (Ventron GmbH), SiO_2 (ABCR Karlsruhe, S_{BET} 266 m²/g), $\gamma\text{-Al}_2\text{O}_3$ (ABCR Karlsruhe, S_{BET} 206 m²/g), silicaaluminas: 87% SiO_2 –13% Al_2O_3 (Ventron GmbH, S_{BET} 392 m²/g) and 53% SiO_2 –45% Al_2O_3 (Ventron GmbH, S_{BET} 114 m²/g). $\text{H}_2\text{SO}_4/\gamma\text{-Al}_2\text{O}_3$ catalysts containing 2, 4, 6, 8 and 9 wt% of H_2SO_4 were obtained using incipient wetness impregnation with sulfuric acid. The obtained preparations were dried at 333 and 383 K for 24 h and then calcined at 753 K in the stream of dry air for another 24 h. In a similar way 53% SiO_2 –45% $\text{Al}_2\text{O}_3\text{-Na}^+$ (1–20 wt% NaOH content) and $\gamma\text{-Al}_2\text{O}_3\text{-Na}^+$ (1–8 wt% NaOH content) catalysts were prepared using NaOH solutions as an impregnating agent. 1.02–1.20 mm grain fraction was used for catalytic measurements.

2.2. Synthesis of styrene dimers

20 g of SiO_2 was initially impregnated with 42 cm³ of 72% H_2SO_4 solution in a 500 cm³ three-neck flask equipped with a magnetic stirrer, a reflux coil condenser and heating mantle then 200 cm³ of styrene added. The reacting system was heated at 383–423 K with stirring for 6 h. The cooled reaction product was placed in separatory funnel. The spent catalyst was washed twice with diethyl ether (2 × 50 cm³) and the solution added to the reaction products. The collected products were washed with sodium hydrogen carbonate solution (2 × 60 cm³) in order to neutralize sulfuric acid. The organic phase was separated and dried with anhydrous calcium chloride, filtered with Buchner funnel and distilled. The resulting product contained polystyrene dimers (91.2 wt%), trimers (7.8 wt%) and tetramers (1.0 wt%). To obtain reaction substrate it was diluted with n-heptane or methylcyclopentane in a 1:1 molar proportion.

2.3. Cumene, styrene dimers and the compounds proposed as polystyrene transition products reactions.

The reactions were performed in a flow reactor. The catalyst (2 cm³) was placed in the reactor and heated for 24 h at 753 K in a stream of dry air. After catalyst activation, the reactor was cooled to the desired temperature (from 473 K to 753 K) and the reactant fed to it with an infusion pump at 3.6 cm³/h for 60 min. Styrene dimers, 4-phenyl-1-butene and n-butylbenzene were fed into reactor as heptane mixtures (1:1 mol). 2-Methyl-1-indene was used as 10 wt% solution in heptane and 2-phenyl-1-indene as 3.6 wt% solution in toluene.

2.4. Diacetone alcohol reactions

The solid acid (0.5 g) was placed in a glass batch reactor (76 cm³) and calcined at 753 K for 20 h in a stream of dry air. The reactor was then cooled to the ambient temperature and the catalyst transferred (in the stream of dry air) into a glass vial (5 cm³) equipped with a screw closure. After the introduction of the substrate (2 cm³) the closed vial was heated up to 313 K for 2 h, cooled and the products analyzed.

2.5. Polystyrene reactions

The reactions were performed in a glass reactor. This was a 15 cm long vial of 20 mm in diameter equipped with a stainless steel mesh 5 cm above the bottom and a joint at the end. 3.0 g of thermoplastic, amorphous polystyrene (average $M_w \sim 230,000$) was initially placed at the bottom of the reactor, then the mesh was placed and 1.5 g of freshly calcined (753 K, 24 h, stream of dry air) catalyst was

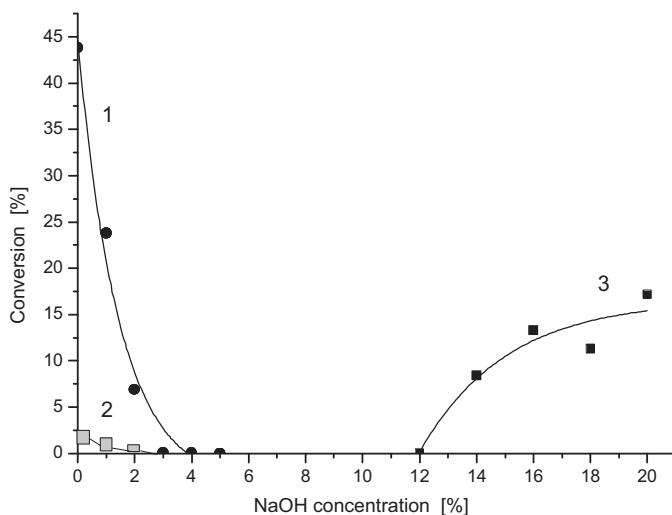


Fig. 1. Acid–base properties of $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%) \text{--Na}^+$ catalysts. Acid properties: cumene to benzene (1) and ethylbenzene (2) conversion (753 K, flow reactor). Basic properties: diacetone alcohol to acetone (3) conversion (313 K, batch reactor).

put on it. The reactor was connected through a distillation adapter equipped with a Liebig condenser and a receiver flask. Finally the reactor was placed in a temperature-controlled tubular electric furnace heated to 753 K. The reaction was completed when liquid products stopped to distill from the reactor (60–90 min).

Thermal transformation of all reactants used was studied replacing a catalyst with the inert silica bed.

2.6. Materials

All organic reactants, sulfuric acid, NaOH , NaHCO_3 , CaCl_2 were supplied by Aldrich.

2.7. Analysis.

The reaction products were analyzed in a GC (Agilent 6890N with FID detector) equipped with a 30 m HP5 capillary column (I.D. 0.32 mm, d_f 0.25 μm , temperature 343 K (5 min), to 543 K at 3 K/min).

3. Results

3.1. The test reactions

The results of cumene (753 K) and diacetone alcohol (313 K) transformation over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%) \text{--Na}^+$ catalysts are presented in Fig. 1.

Cumene reaction was observed solely for the catalysts containing less than 4% of sodium ions. Benzene and ethylbenzene were the main reaction products. Diacetone alcohol began to react only when the surface concentration of NaOH exceeded 12%. The only product observed was acetone.

The results of the test reactions over alkalinized and sulfated alumina are shown in Fig. 2. At 753 K cumene practically did not react in the presence of $\gamma\text{-Al}_2\text{O}_3\text{--Na}^+$ catalysts. Only pure alumina initiated the reaction resulting in the formation of benzene and ethylbenzene at conversions of 0.6% and 0.3% respectively. Diacetone alcohol, however, reacted at 313 K giving 3% conversion into acetone for undotted $\gamma\text{-Al}_2\text{O}_3$ and 95% for the catalysts with NaOH concentration higher than 1%.

Sulfated alumina is a very strong acid [59] so the cumene test reaction was performed at a low temperature, i.e. 573 K. The introduction of 2 wt% of H_2SO_4 on alumina surface initiated cumene

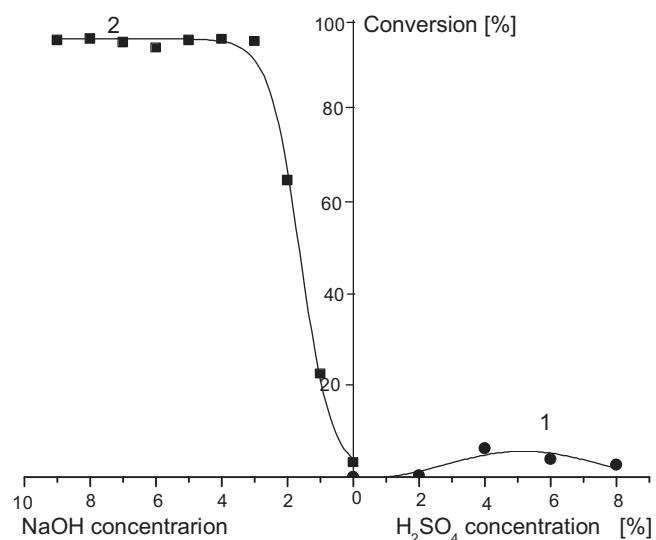


Fig. 2. Acid–base properties of $\gamma\text{-Al}_2\text{O}_3\text{--H}_2\text{SO}_4$ and $\gamma\text{-Al}_2\text{O}_3\text{--Na}^+$ catalysts. Acid properties: cumene to benzene and diisopropylbenzene (1) conversion (573 K, flow reactor). Basic properties: diacetone alcohol to acetone (2) conversion (313 K, batch reactor).

reaction resulting in the formation of disproportionation products, i.e. benzene and diisopropylbenzenes (Fig. 2).

3.2. Polystyrene and styrene dimers reactions

The results of the transformation of styrene and styrene dimers over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%) \text{--Na}^+$, $\gamma\text{-Al}_2\text{O}_3\text{--Na}^+$ and $\gamma\text{-Al}_2\text{O}_3\text{--H}_2\text{SO}_4$ at 753 are gathered in Tables 1 and 2.

Silicaalumina as well as silicaalumina dotted with NaOH up to 2 wt% catalyzed polystyrene cracking leading to styrene, ethylbenzene, toluene, benzene, α -methylstyrene, indane, indene, 1,1- and 1,2-diphenylpropenes, naphthalene and isomerized dimers and trimers of styrene. In the presence of $\gamma\text{-Al}_2\text{O}_3\text{--H}_2\text{SO}_4$ (1–9%) catalysts the main reaction products were: styrene, ethylbenzene, toluene, benzene, α -methylstyrene and isomerized dimers and trimers of styrene. The decomposition of polystyrene performed over basic catalysts, i.e. $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%) \text{--Na}^+$ (NaOH : 14–18 wt%), $\gamma\text{-Al}_2\text{O}_3\text{--Na}^+$ (NaOH : 4–6 wt%) resulted in the formation of similar products. However, indane, indene, 1,1- and 1,2-diphenylpropenes as well as naphthalene were not observed among the reaction products.

The results of the reactions of styrene dimers dissolved in heptanes (mole ratio 1:1) over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%) \text{--Na}^+$ at 753 K are presented in Table 3.

The transformation of styrene dimers led to the same products as observed for polystyrene cracking over the same catalysts. The main difference was in the respective product selectivities. For example selectivity towards styrene was much lower in the case of styrene dimers reaction (3–20%) than for polystyrene transformation (62–85%). Higher selectivities were also observed for indane, indene, methyl derivatives of indane and indene, 1,1- and 1,2-diphenylpropenes, naphthalene and methylnaphthalenes. In a manner similar to polystyrene transformation a decrease of some reaction products, i.e. for indane, indene, methyl derivatives of indane and indene, 1,1- and 1,2-diphenylpropenes, naphthalene with an increase in the content of NaOH on silicaalumina surface can be observed. Moreover styrene dimers apart of decomposition underwent isomerization. The selectivity of this reaction also increased with an increase in the concentration of sodium on the catalysts.

Table 1Polystyrene transformation over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%)$ – Na^+ catalysts. Reaction temperature 753 K.

Sodium concentration (%)	0	1	2	6	12	18	Therm ^a	S-A(13) ^b
	Products selectivity (%)							
benzene	2.9	1.3	0.3	0.1	0.2	0.2	0.2	18.2
toluene	3.3	3.8	3.7	2.9	2.0	2.1	4.6	5.9
ethylbenzene	13.5	7.5	3.1	0.6	0.2	0.2	1.3	42.4
styrene	62.3	76.2	82.3	84.3	82.7	83.7	84.6	11.2
cumene	0.9	0.6	0.3	–	–	–	–	4.8
α -methylstyrene	5.5	5.7	6.0	3.0	1.1	1.2	3.1	2.6
indane + indene	0.1	–	–	–	–	–	–	2.1
1,1-diphenylpropane + 1,1-diphenylpropene	1.4	0.7	0.6	0.6	0.5	0.5	–	1.6
1,2-diphenylpropane + 1,2-diphenylpropene	1.3	0.3	0.2	–	–	–	–	0.1
naphthalene	0.2	–	–	–	–	–	–	1.1
dimer	6.2	2.8	2.4	5.7	7.3	7.3	3.7	4.1
trimer	0.9	0.4	0.1	2.4	5.0	4.3	1.0	–
Conversion (%)	58.6	65.5	57.9	62.4	68.2	66.3	69.8	60.5

^a PS thermal transformation (SiO_2 was used instead of a catalyst).^b PS transformation over $\text{SiO}_2\text{--Al}_2\text{O}_3(13\%)$.**Table 2**Polystyrene transformation over $\gamma\text{-Al}_2\text{O}_3\text{--Na}^+$ and $\gamma\text{-Al}_2\text{O}_3\text{--H}_2\text{SO}_4$ catalysts. Reaction temperature 753 K.

Al_2O_3 modicator	NaOH		H_2SO_4			MgO^a		
	6	4	0	1	3	6	9	
	Products selectivity (%)							
benzene	0.1	0.1	0.4	0.4	0.9	0.6	0.9	0.2
toluene	3.3	3.6	6.7	4.9	5.0	5.7	5.6	4.9
ethylbenzene	1.5	2.5	8.8	10.0	14.8	17.5	15.8	0.6
styrene	90.3	87.4	71.8	71.9	65.6	60.9	63.3	86.9
cumene	–	–	0.4	0.6	0.9	0.9	1.0	0.1
α -methylstyrene	1.6	1.6	7.3	7.3	7.5	8.2	8.3	2.7
1,1-diphenylpropane+1,1-diphenylpropene	0.3	0.4	0.7	0.8	1.0	1.3	1.0	0.3
1,2-diphenylpropane+1,2-diphenylpropene	–	–	–	0.1	–	0.1	–	–
dimer	2.0	3.5	2.5	3.4	3.2	3.8	2.2	3.1
trimer	0.2	0.1	–	–	–	–	–	0.7
Conversion (%)	66.7	58.1	68.6	63.0	60.4	60.9	59.3	75.1

^a PS transformation over MgO .

The influence of the nature of the solvent on the transformation of styrene dimers was also studied. The results obtained in the presence of inert heptane and hydrogen donating methylcyclopentane over $\text{SiO}_2\text{--Al}_2\text{O}_3(13\%)$ catalyst at 753 K are presented in Table 4.

The results indicate that in the presence of methylcyclopentane the total conversion and product selectivity of styrene dimers changes. Total conversion rose from 48.5% to 69.5%. The most significant selectivity change was noticed for ethylbenzene, which increased from 32.6% to 40.9%.

3.3. Transition products of polystyrene and styrene dimers reactions

The reactions of 2-phenylindene, 2-methyl-1-indene, n-butylbenzene and 4-phenyl-1-butene over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%)$ at 753 K were studied (Table 5).

It was found that n-butylbenzene, 4-phenyl-1-butene and 2-methyl-1-indene reacted in a similar manner as styrene dimers. Benzene and indane were the main reaction products of 2-phenylindene transformation.

Table 3Styrene dimers transformation over $\text{SiO}_2\text{--Al}_2\text{O}_3(45\%)$ – Na^+ catalysts. Reaction temperature 753 K, reactant: dimer/heptane (1:1), LHSV: 1.86 h⁻¹.

Sodium concentration on S-A(45) (%)	0	1	2	6	14	18	Therm ^a
	Products selectivity (%)						
benzene	14.0	7.4	2.4	0.3	0.9	0.4	1.0
toluene	7.0	6.3	8.4	8.4	2.8	2.5	3.9
ethylbenzene	37.8	34.8	29.9	10.0	11.0	10.1	7.8
styrene	2.8	8.3	19.8	11.0	12.3	8.6	19.8
cumene	4.0	3.8	3.1	1.0	0.4	0.0	0.4
n-propylbenzene	1.7	0.5	1.2	0.5	0.9	0.4	–
α -methylstyrene	1.3	2.9	6.7	9.8	3.0	2.9	4.4
indane+indene	2.8	1.1	0.2	–	–	–	0.5
methylindane+methylindene	–	3.8	1.4	–	–	–	–
1,1-diphenylpropane+1,1-diphenylpropene	5.9	1.4	2.4	0.7	–	0.4	0.6
1,2-diphenylpropane+1,2-diphenylpropene	1.0	0.5	1.0	1.7	0.9	0.8	2.7
naphthalene	2.6	0.5	–	–	–	–	–
methylnaphthalenes	0.5	0.7	0.8	0.3	–	–	–
dimers	16.0	26.9	20.8	54.6	65.7	74.7	53.4
Conversion (%)	57.3	55.9	49.2	59.2	46.3	48.5	35.4

^a Oligomer thermal transformation.

Table 4

Styrene dimers transformation over $\text{SiO}_2\text{-Al}_2\text{O}_3$ (13%) catalyst. Reaction temperature 753 K, reactant: dimer/heptane and dimer/methylcyclopentane (1:1), LHSV: 1.86 h^{-1} .

Styrene dimers solvent	heptane	methylcyclopentane
Product selectivity (%)		
benzene	33.8	26.9
toluene	3.8	4.4
ethylbenzene	32.9	40.9
styrene	1.9	1.3
cumene	0.8	0.4
n-propylbenzene	0.7	0.5
α -methylstyrene	–	–
indane+indene	3.7	3.9
methylindane+methylindene	6.6	10.3
1,1-diphenylpropane+1,1-diphenylpropene	–	–
1,2-diphenylpropane+1,2-diphenylpropene	–	–
naphthalene	7.7	5.6
methylnaphthalenes	2.1	2.2
dimers	3.3	3.5
Conversion (%)	48.5	69.5

4. Discussion

Catalytic decomposition of polystyrene is initiated by solid acids and bases. Polystyrene undergoes two main reactions in both cases: a stepwise depolymerization and polymer decomposition into oligomers followed by their consecutive cracking. It was shown that basic catalysts catalyze polystyrene decomposition according to selective depolymerization pathway whereas over solid acids a pathway leading to products other than styrene is preferred [29,50,53]. In order to understand better polystyrene transformation it is necessary to consider not only the catalyst nature but also the type of the reactor used. In the presented work it was a batch reactor with continuous output of gaseous decomposition products. Since the catalyst bed was placed on a stainless steel mesh above the polystyrene load it is evident that only polystyrene thermal decomposition products, volatile at 753 K, could react. Such products were styrene oligomers like dimers, trimers or tetramers. A comparison of the results of the decomposition of polystyrene and styrene oligomers (mostly dimers, Tables 1 and 3) shows that styrene which is the main product of polystyrene cracking over $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%)- Na^+ catalysts is formed from dimers with low selectivity varying from 2% to 20%. This means that oligomers higher than polystyrene dimers (trimers, tetramers) are the proper substrates of polystyrene catalytic transformation which leads to high styrene selectivity, i.e. 26–85%. It has already been postulated that the styrene trimer (triphenylhexane) can be considered to be the substrate [53].

Table 5

n-Butylbenzene (n-BB), reactant/heptane (1:1); 4-phenyl-1-butene (4-Ph-1-butene), reactant/heptane (1:1); 2-methyl-1-indene (2-Me-1-indene), reactant/heptane (1:10) and 2-phenyl-1-indene (2-Ph-1-indene), (3.6 wt% in toluene) transformation over $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%) catalyst. Reaction temperature 753 K, LHSV: 1.86 h^{-1} .

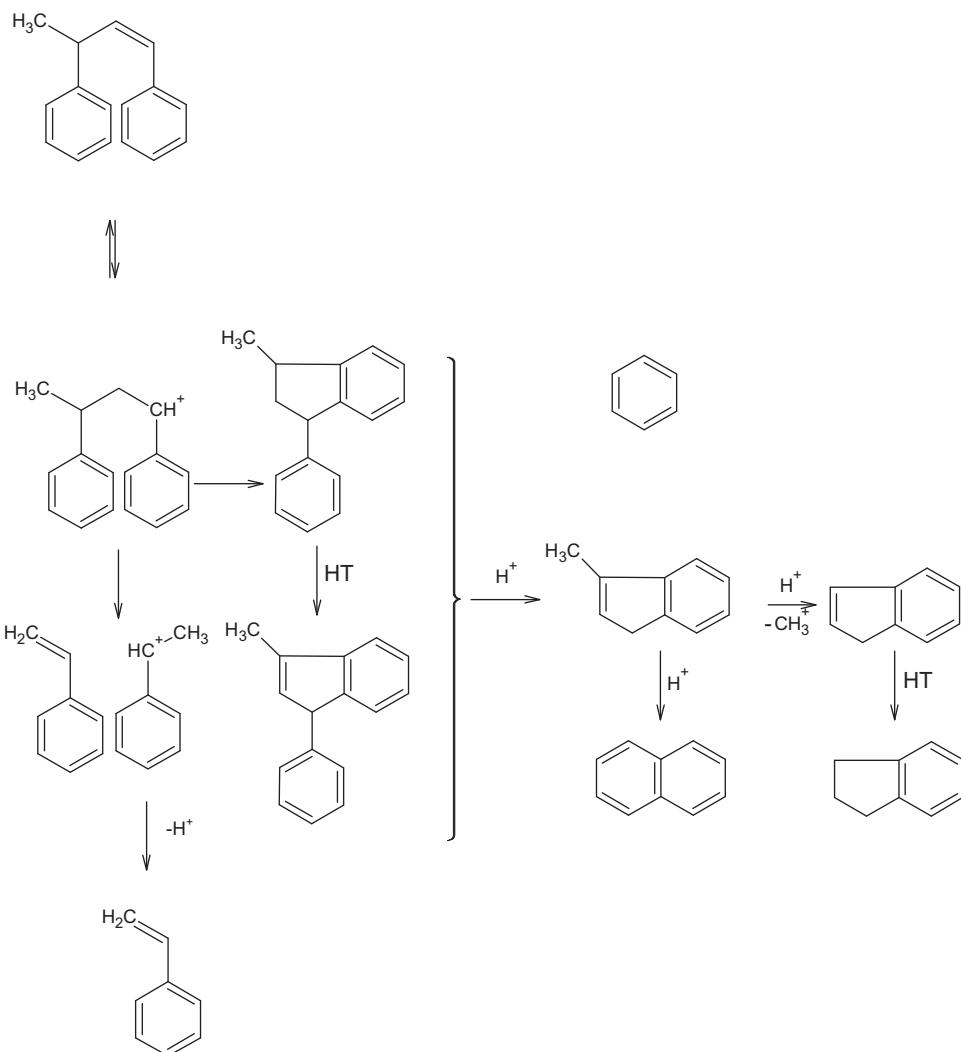
Reactant	n-BB	4-Ph-1-Butene	2-Ph-1-Indene	2-Me-1-Indene
main products selectivity (%)				
benzene	39.5	14.6	a	20.9
toluene	12.0	10.4	b	5.4
ethylbenzene	4.4	3.0	–	1.9
styrene	0.9	0.4	–	–
indane + indene	1.2	2.8	49.5	2.1
methylindane + methylindene	7.3	19.1	–	4.2
tetraline	–	0.4	–	–
naphthalene	8.6	20.6	–	25.7
methylnaphthalenes	8.3	12.1	–	10.6
Conversion (%)	42.7	62.3	12.7	77.6

^a Benzene was detected among reaction products but it could result from toluene reactions.

^b Toluene was used as a solvent.

The obtained results make the evaluation of the influence of acid and base centers on polystyrene catalytic transformation possible. The catalysts used were prepared by the modification of two carriers. These were silicaalumina with Al_2O_3 content equal to 45% possessing both Brønsted and Lewis acid sites and $\gamma\text{-Al}_2\text{O}_3$ – a strong Lewis acid [60]. In order to modify their acid–base characteristics both oxides were dotted with NaOH. Such treatment results in the simultaneous elimination of acid centers and the formation of basic sites [61]. In the case of alumina the catalysts containing different amount of sulfuric acid were also synthesized. It is known that the sulfation substantially increases acid strength of the alumina [56]. It has even been reported that this can be considered a superacid [56]. In order to study the influence of the introduction of NaOH on the surface of silicaalumina and alumina as well as H_2SO_4 on alumina surface on acid–base properties of these systems test reactions with cumene and diacetone alcohol were performed (Figs. 1 and 2). It can be seen that catalytic system $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%)- Na^+ changes its nature from acidic (0–4% of NaOH) to basic (>12 wt% NaOH) depending on NaOH content. The catalysts with low concentration of sodium ions concentration catalyze cumene transformation while those with higher NaOH load initiate diacetone alcohol reactions. The catalysts based on $\gamma\text{-Al}_2\text{O}_3$ as support possess basic properties (0–8 wt% NaOH) allowing diacetone alcohol reaction initiation and acid ones (1–9 wt% H_2SO_4) which permit to catalyze cumene transformation. Polystyrene transformation was then studied over the characterized catalysts. It was found that polystyrene decomposes to benzene, indane and indene, naphthalene and diphenyl derivatives of propane and propene in the presence of acid catalysts ($\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%) and $\text{SiO}_2\text{-Al}_2\text{O}_3$ (13%)). Catalyst selectivity towards these products decreased with an increase in the concentration of NaOH on the surface $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%) surface and raise in H_2SO_4 content on the surface of alumina. A similar phenomenon was observed in the case of the transformation of styrene dimers over $\text{SiO}_2\text{-Al}_2\text{O}_3$ (45%)- Na^+ catalysts (Table 3). It seems therefore, that the reaction products can be formed as a result of styrene dimers transformation (Schemes 3 and 4). One can consider two reaction sequences. The first (A) begins with Brønsted acid center attack on aliphatic chain of styrene dimer while the second (B) starts from a proton addition to the aromatic ring of the dimer.

A. Proton attachment to the double bond of styrene dimer results in the formation of a carbenium ion, which undergoes decomposition (β -cleavage) to styrene cyclization resulting in methyl-phenyl-indane formation. Under the action of Brønsted acid sites it form respective carbenium ion which, in consecutive reactions sequence (dealkylation, isomerization and hydrogen transfer), give benzene, methylindene and methylindane, indene and indane, naphthalene and diphenylpropane and diphenylpropene. In order to confirm the possibility of such



Scheme 3.

transformation 2-phenylindene and 2-methyl-1-indene were passed over SiO₂–Al₂O₃(45%) catalyst (Table 5). These compounds are either present in the proposed reaction scheme for styrene dimers (2-methyl-1-indene) or possess a similar structure as transition reaction products (2-phenylindene). 2-Phenylindene reacted with benzene, indane and indene formation. Such products could be formed if other reaction such as hydrogen transfer took place apart from substrate protonation and then dealkylation. 2-Methyl-1-indene underwent isomerization and acid–base dehydrogenation to naphthalene as well as dealkylation and coking (Table 5, Scheme 4). The presented results confirm the proposed reaction scheme (Scheme 3) for the transformation of styrene dimers.

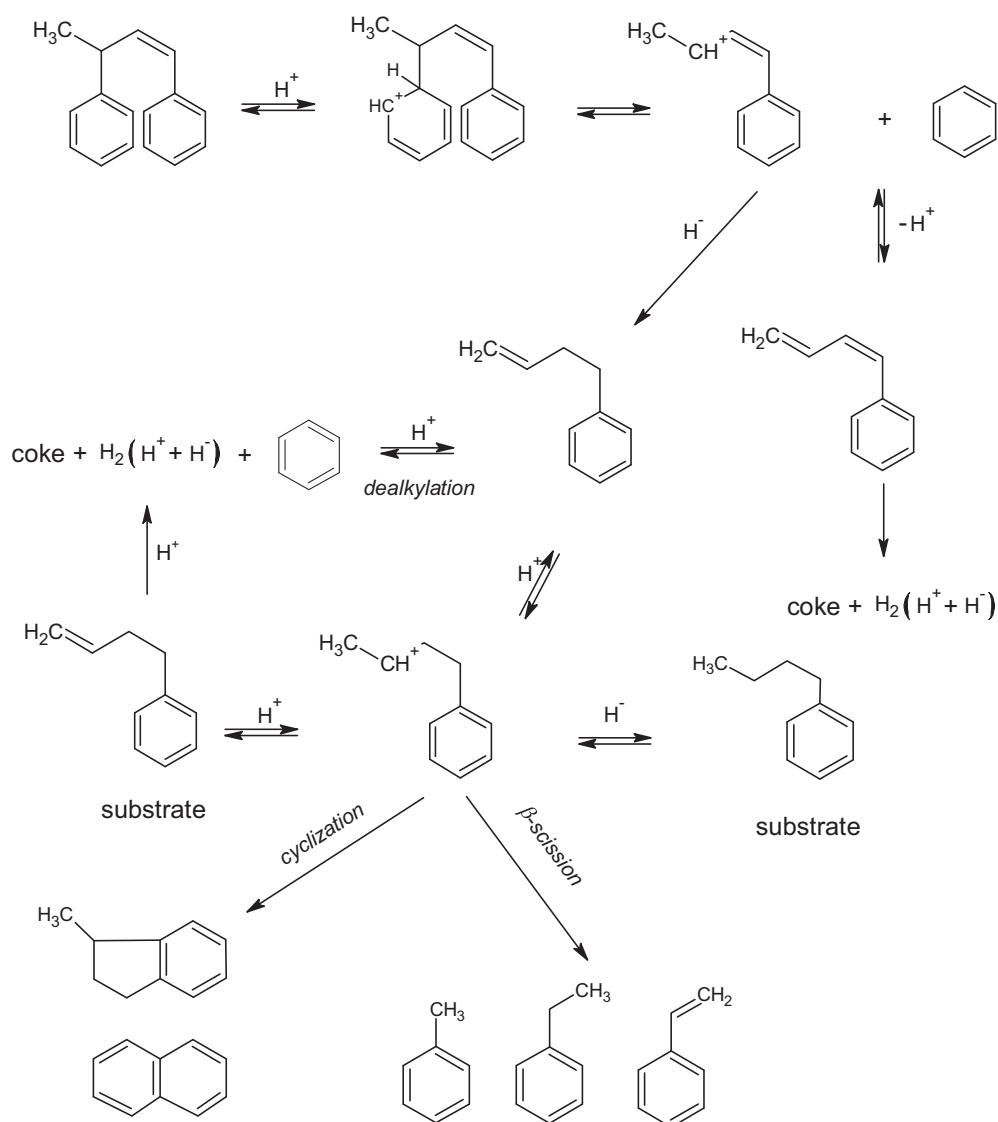
B. The second reaction sequence of styrene dimers starts also from the attack of Brønsted acid sites on aromatic ring rather than on the aliphatic chain (Scheme 4).

The resulting carbenium ion undergoes dealkylation resulting in benzene and alkanyl aromatic cation. The latter compound either reacts with a hydride anion gives phenylbutene or to phenylbutadiene – the coke precursor after proton detachment. The formed phenylbutene can undergo protonation either in aromatic ring which results in dealkylation or in the aliphatic chain which initiates further transformation. In order to further study the mechanism some additional experiments with 4-phenyl-1-butene and n-butylbenzene as reactants were performed (Table 5). It was found that two main reactions occur: internal cyclization and side chain

cracking. The former reaction results in indane and naphthalene derivatives while the latter produces toluene, ethylbenzene and styrene. Since the similar reaction products were observed during styrene dimers transformation it can be concluded that the proposed reaction schemes (Schemes 3 and 4) take place during polystyrene degradation over acid catalysts. Another phenomenon that confirms the proposed mechanism is that with a rise in the concentration of NaOH concentration on the silicaalumina surface which results in a simultaneous decrease of the number of acid sites active in these reactions, the selectivities of discussed products decrease. The relation between respective selectivities of polystyrene dimers reaction products and catalyst acidity for SiO₂–Al₂O₃(45%)–Na⁺ system is presented in Fig. 3.

Cumene to benzene conversion at 753 K was taken as a measure of the acid properties of the studied catalysts. The observed linear relationship confirms the role of Brønsted acid centers in the postulated mechanism of the reaction (Scheme 3).

Similar reactions involving polystyrene transformation were presented by Lin et al. They had studied the transformation of a polystyrene solution adsorbed on acid catalysts, i.e. SiO₂–Al₂O₃ (11.8 wt%), HZSM-5 (Al₂O₃ 1.5 wt%) and ZrO₂/SO₄²⁻ as a thermoprogrammed reaction [50]. It was proposed that transformation begins with proton attack on the aromatic ring of polystyrene. The resulting carbenium ion undergoes dealkylation to form benzene and a new cation which further decomposes. Our results indicate



Scheme 4.

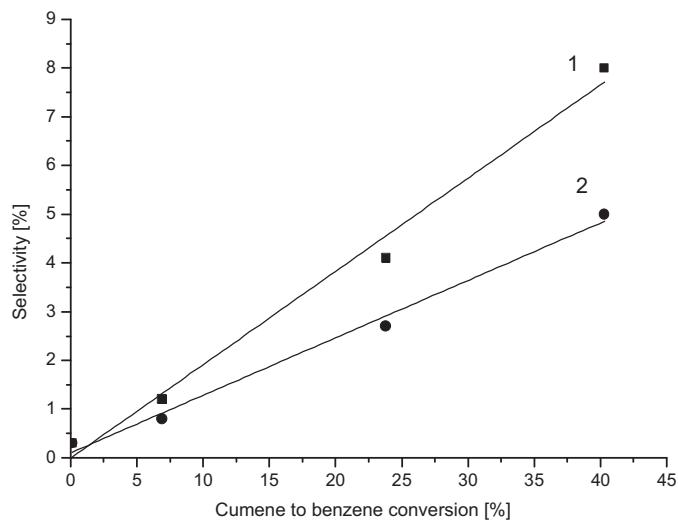
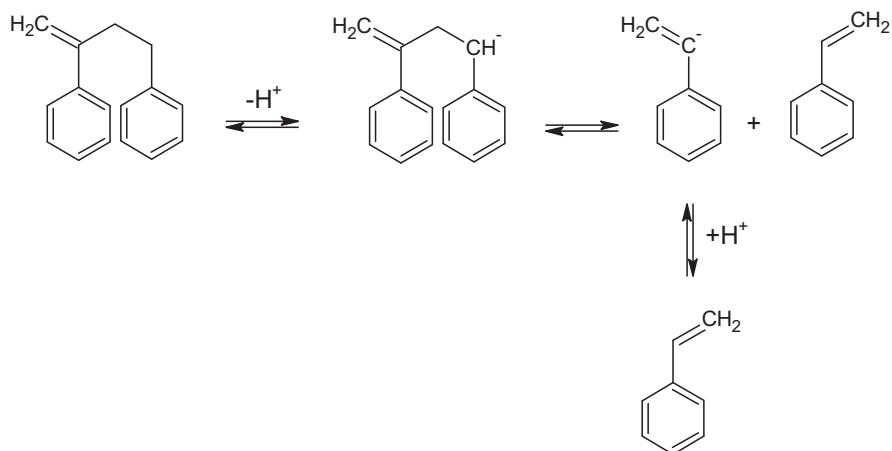


Fig. 3. The influence of catalyst acidity on styrene dimers transformations. Benzene selectivity (1), a sum of indane and indene derivatives selectivity (2). Catalysts: $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)-\text{Na}^+$.

that styrene oligomers are substrates for catalytic polystyrene transformation.

Styrene end ethylbenzene, the most important polystyrene decomposition products, are formed as a result of the cracking of higher styrene oligomers. Both acid and base centers catalyze this reaction. As illustrated in Fig. 4 the conversion of styrene dimers into styrene and ethylbenzene is plotted vs. NaOH concentration for $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)-\text{Na}^+$ catalysts.

In the range of low NaOH concentration (0–5 wt%) the yield to ethylbenzene and styrene diminishes proportionally from 23% to 10%. This indicates the catalytic activity of Brønsted acid centers which prevail in such NaOH content. A further increase in the loading of sodium ions results in a change in the nature of the silicaluminia surface from acidic to basic. This phenomenon leads to a change in the reaction mechanism and causes the step change in the relation as presented in Fig. 4. The total conversion of ethylbenzene and styrene increases from 10% for $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)-\text{Na}^+(5\%)$ catalyst to 12% for the catalyst with 6% of NaOH. A further increase in the concentration of NaOH on the surface results in a slight decrease in conversion to 10% for the $\text{SiO}_2\text{-Al}_2\text{O}_3(45\%)-\text{Na}^+(20\%)$ catalyst. The differences in the mechanism of polystyrene decomposition are also reflected in the respective values of ethylbenzene to styrene ratio for $\gamma\text{-Al}_2\text{O}_3\text{-Na}^+$ and $\gamma\text{-Al}_2\text{O}_3\text{-H}_2\text{SO}_4$ catalysts (Fig. 5).



Scheme 5.

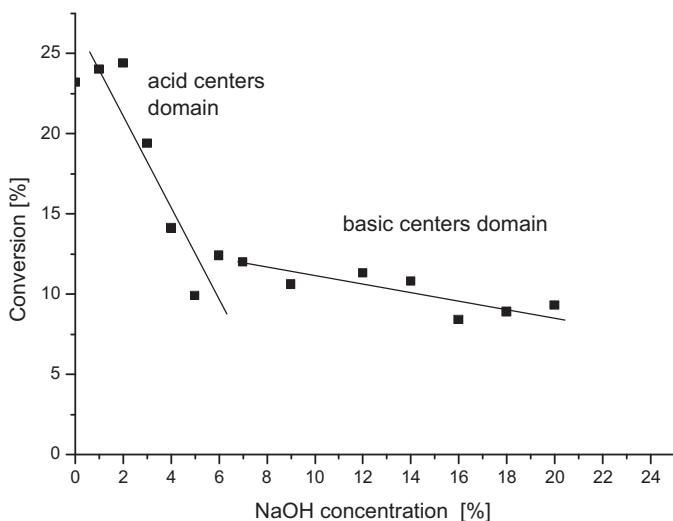


Fig. 4. The influence of catalyst basicity on styrene dimers conversion into styrene and ethylbenzene. Catalysts: $\text{SiO}_2-\text{Al}_2\text{O}_3(45\%)-\text{Na}^+$.

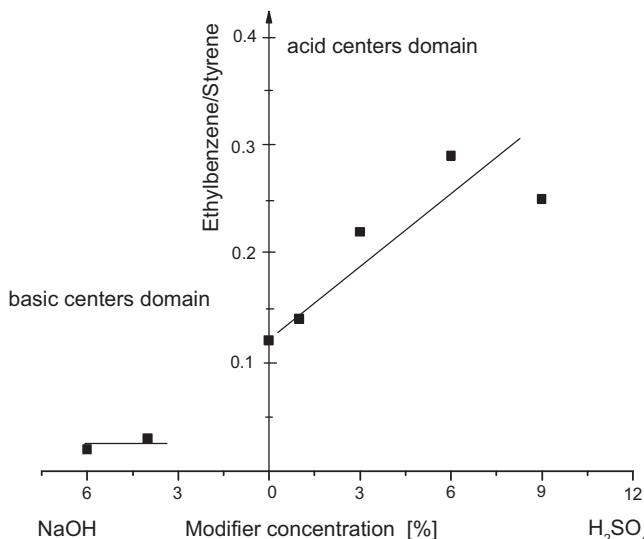
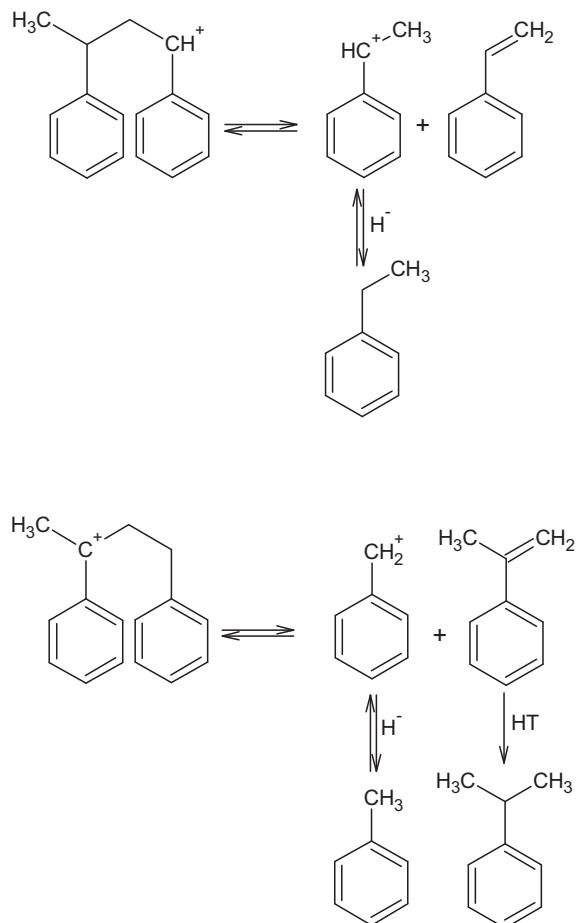


Fig. 5. The influence of acid and basic properties of $\gamma\text{-Al}_2\text{O}_3-\text{H}_2\text{SO}_4$ and $\gamma\text{-Al}_2\text{O}_3-\text{Na}^+$ catalysts on ethylbenzene/styrene ratio in styrene dimers transformations.

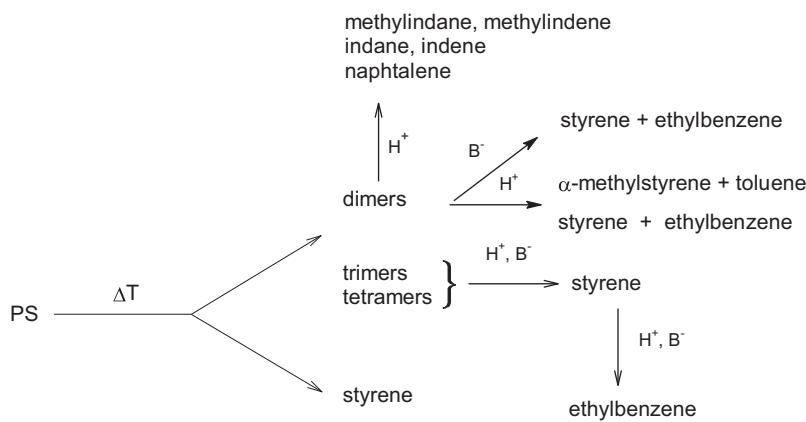
For the basic catalysts selective depolymerization of styrene dimers takes place. The possible mechanism is presented in the Scheme 5 for styrene dimers as a substrate [53].

For acid-type catalysts the rise of ethylbenzene conversion in relation to styrene can be observed. Ethylbenzene is the most probably formed in two reactions: styrene dimers cracking and consecutive styrene hydrogenation (Scheme 6).

The later reaction can be treated as a hydrogen transfer of H^+ and H^- ions formed during catalyst coking reactions [62]. Since coking readily in the presence of Brønsted acid sites then the observed



Scheme 6.



Scheme 7.

higher ethylbenzene/styrene ratio for $\gamma\text{-Al}_2\text{O}_3\text{-H}_2\text{SO}_4$ catalyst is reasonable. A similar relationship can be observed for toluene and α -methylstyrene selectivities for $\gamma\text{-Al}_2\text{O}_3\text{-Na}^+$ and $\gamma\text{-Al}_2\text{O}_3\text{-H}_2\text{SO}_4$ catalysts for polystyrene decomposition (Fig. 6).

For base catalysts, i.e. $\gamma\text{-Al}_2\text{O}_3$ – 4–6 wt% NaOH the selectivity for the formation of both product is low. Unmodified alumina possessing Lewis acid centers is capable of withdrawing a hydride ion from polystyrene forming polystyrene cation – PS⁺ (Scheme 2). These species undergo a series of transformations characteristic to acid catalyzed cracking leading to coke formation apart of observed reaction products. During coke formation, H⁺ and H⁻ ions are generated, which can be consumed in toluene formation (Scheme 6). This results in a dramatic increase in toluene and α -methylstyrene selectivities. The introduction of H₂SO₄ on alumina surface results in the formation of new Brønsted acid sites and a new relationship is observed as presented in Fig. 6. These centers accelerate polystyrene cracking and facilitate, due to coking reactions, hydride ion transfer to the benzyl cation (Scheme 6) – a step which is necessary for toluene creation. An additional confirmation of the importance of hydrogen transfer reaction on polystyrene cracking results was found in experiments where heptane was replaced by methylcyclopentane as a solvent for styrene dimers. The later compound due to presence of III-rd order carbon atom is an effective donor of hydride anion. The reaction was performed in the presence

of SiO₂–Al₂O₃(13%), a catalyst with strong acid properties. Ethylbenzene to styrene ratio obtained for methylcyclopentane dimers solution was equal to 31.4 while for n-heptane only 17.3 (Table 4). Thus, the low styrene selectivity observed for acid catalysts is probably caused by its consecutive hydrogenation in hydrogen transfer reactions.

A general scheme of polystyrene decomposition catalyzed by acid catalysts (H⁺) and base catalysts (B⁻) taking place in semi continuous batch reactor can therefore be proposed (Scheme 7).

The first step in the thermal decomposition of polystyrene consists of two main reactions: depolymerization, leading to the formation of styrene and degradation to volatile oligomers. The latter reaction takes place due to a hydrogen shift along carbon chain of polystyrene radical. Further transformation takes place under the influence of acid or basic centers of a catalyst. Styrene oligomers are the proper substrates. These oligomers react in different way depending on the chain length. Linear dimers undergo decomposition to styrene and ethylbenzene as well as toluene and α -methylstyrene. Acid catalysts catalyze coke formation, accompanied by H⁺ and H⁻ ions production, as well as hydrogen transfer which causes styrene hydrogenation to ethylbenzene. In the presence of basic catalysts the transformation leading to a coke is slower and ethylbenzene formation is suppressed. This is why a lower styrene selectivity was observed for acid catalysts in comparison with their basic counterparts. In the presence of acid catalysts linear dimers can also isomerize to cyclic derivatives to obtain benzene and methylindane after dealkylation. The later product on isomerization and hydrogen transfer reactions forms methylindene and naphthalene. Higher styrene oligomers react in the presence of both acid and basic active centers and are mainly responsible for styrene formation. In the presence of acid catalysts styrene selectivity is lowered due to hydrogen transfer reaction resulting in ethylbenzene formation.

5. Conclusions

The chemistry of polystyrene recycling is of a complex nature since it consists of both thermal and catalytic transformation. The first case involves two main reaction pathways: gradual depolymerization to the monomer (styrene) and pyrolysis leading to the formation of different volatile oligomers (dimers, trimers, tetramers.). The latter species react solely over the catalyst active centers. Styrene linear dimers undergo decomposition to styrene and ethylbenzene as well as to toluene and α -methylstyrene over Brønsted acid sites. Consecutive transformation of the products leads to coke formation with simultaneous hydrogen (H⁺ and H⁻) production. The latter ions are active in hydrogen transfer reactions which results in hydrogenation of styrene to ethylbenzene. In the

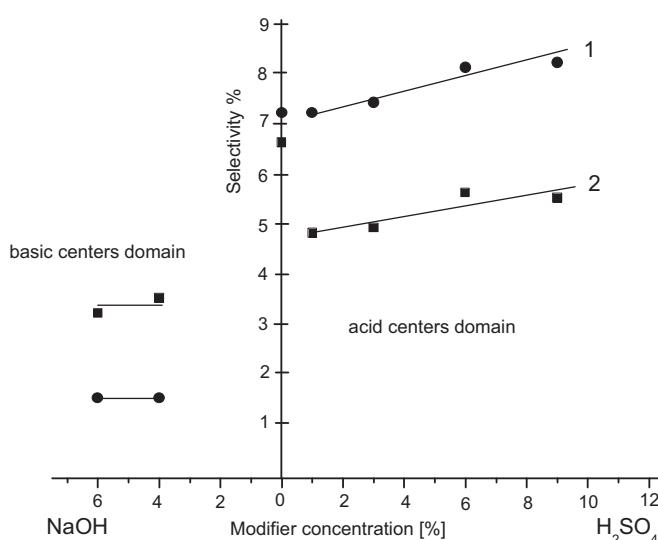


Fig. 6. The influence of acid and basic properties on $\gamma\text{-Al}_2\text{O}_3\text{-H}_2\text{SO}_4$ and $\gamma\text{-Al}_2\text{O}_3\text{-Na}^+$ catalysts on the selectivity of α -methylstyrene (1) and toluene (2) formation in the polystyrene transformation.

presence of base catalysts selective styrene formation takes place and the transformation leading to coke is slower hence ethylbenzene formation is suppressed. This is the reason for lower styrene selectivity observed for acid catalysts in comparison with basic species. In the presence of acid catalysts linear dimers can also isomerizes to cyclic derivatives to produce benzene and methylindane after dealkylation. The later product in isomerization and hydrogen transfer reactions forms methylindene and naphthalene. The reactions of higher oligomers are catalyzed by acid and basic sites giving mainly the monomer, i.e. styrene formation.

Acknowledgment

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